Development of High Efficiency Thermoelectric Materials and Unicouples for Power Generation Applications

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The efficiency of current solid state thermoelectric coolers and power generators is primarily limited by the relatively low efficiency of the thermoelectric materials used to fabricate these devices. A brief review of state-of-the-art thermoelectric materials both for cooling and power generation is given. A considerable amount of research has been performed over the last decade to develop new efficient thermoelectric materials. Promising results have been obtained and new materials with superior thermoelectric properties have been discovered. Some of the new materials under development are introduced in this paper. Highly efficient, segmented thermoelectric unicouples incorporating advanced thermoelectric materials with superior thermoelectric figures of merit are currently being developed at the Jet Propulsion Laboratory (JPL). These segmented unicouples include a combination of state-of-the-art thermoelectric materials based on Bi_2Te_3 and novel p-type Zn_4Sb_3, p-type $CeFe_4Sb_{12}$-based alloys and n-type $CoSb_3$-based alloys developed at JPL. The maximum predicted thermal to electrical efficiency is about 15% for a hot-side temperature of 975K and a cold-side temperature of about 300K. Several unicouples with different segmentation are currently being fabricated and tested at JPL. Experimental thermal to electrical efficiency values of about 10% have been demonstrated. These advanced unicouples could be used in a variety of power generation applications including waste heat recovery and space. These applications are briefly reviewed.

1. Introduction

Thermal energy can be converted into electricity and electricity can be used for heat pump or refrigeration using the Seebeck and Peltier thermoelectric effects, respectively. For cooling applications, an electrical current flows through a thermoelectric material and heat is absorbed at the cold side and rejected at the sink (Fig. 1a). Imposing a temperature difference across a unicouple schematically represented in Fig. 1b will generate an electrical current driven through the load.

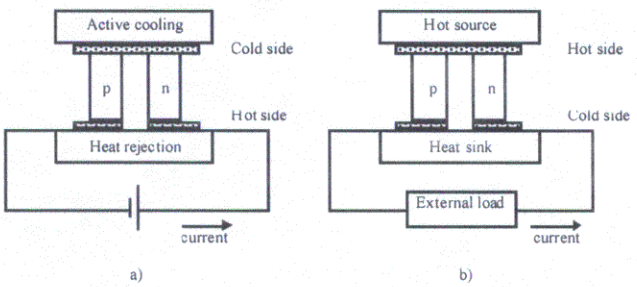

Fig. 1 Schematic diagram of a single thermocouple configured for refrigeration (a) or power generation (b). The thermoelectric couple consists of one p- and one n- type semiconducting branches. Actual thermoelectric devices are typically composed of a plurality of such thermoelectric couples connected electrically in series and thermally in parallel to form a module. When an electric current is passed through the module, heat is absorbed at one side (cold side) of the module and rejected at the other side (hot side) and the device operates as a cooler. Conversely, if an external temperature difference is applied to the module, electrical power will be delivered to an external load and the device operates as a power generator.

The efficiency of thermoelectric devices primarily depends on a material's factor, Z, known as the figure of merit and defined as:

$$Z = \frac{\alpha^2}{\rho\lambda} \qquad (1)$$

where α is the Seebeck coefficient, ρ the electrical resistivity, and λ the thermal conductivity of the thermoelectric material The larger Z is, the larger the conversion efficiency is. The dimensionless figure of merit ZT is often preferred to Z. The best ZT materials are typically heavily doped semiconductors because they clearly offer the most possibilities for achieving reasonably high Seebeck coefficient with moderately low thermal conductivity and electrical resistivity. In the following sections, we briefly introduce state-of-the-art thermoelectric materials, review recent developments on new materials, and illustrate recent efforts at the Jet Propulsion Laboratory (JPL) to incorporate some of these new materials into advanced power generation unicouples.

2. State-of-the-art thermoelectric materials

Many materials have investigated as potential thermoelectric materials since the 1950's. ZT values for materials considered state-of-the-art are shown in Fig. 2. Comprehensive reviews for state-of-the-art thermoelectric materials can be found, for example, in Refs. 1 and 2.

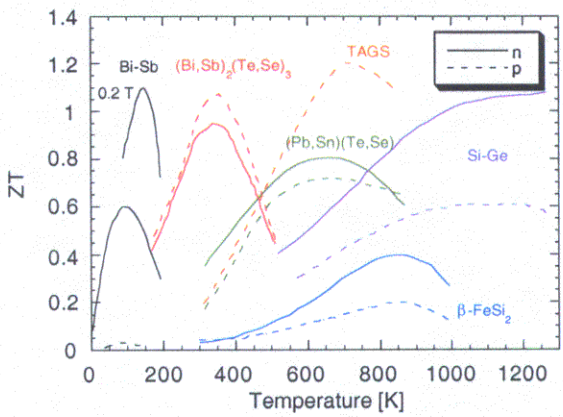

Fig. 2 Temperature dependence of the dimensionless figure of merit ZT as a function of temperature for several n- and p- type state-of-the-art materials.

Near room temperature, the most useful materials are $(Bi,Sb)_2(Te,Se)_3$ alloys. N- and p-type materials can be obtained through alloying and/or doping. Because these materials have a fairly small band gap (~ 0.16 eV for Bi_2Te_3), they are not useful materials above ~ 500K. Below room temperature, thermoelectric cooling is less efficient because ZT mainly decreases as a result of the increase in lattice thermal conductivity. For temperatures lower than 220K, n-type Bi-Sb alloys become superior to $(Bi,Sb)_2(Te,Se)_3$ alloys. Undoped Bi-Sb alloys are always n-type. P-type alloys can be produced by doping. Unfortunately, due to the peculiarities of the complex valence band structure, p-type alloys have rather low ZT values.

Materials to be used in power generators should be chemically stable at high temperatures and have a band gap large enough to minimize minority carrier conduction at high temperatures and prevent a decrease in the Seebeck coefficient. PbTe alloys satisfy these requirements and are the most useful materials in the 500-800 K temperature range. PbTe can be made n- or p-type by varying the stoichiometry. The figure of merit of PbTe can be improved by the formation of solid solutions. More complex compounds, formed by alloying $AgSbTe_2$ with GeTe, and referred to as TAGS compounds, have been proven to be effective p-type materials in the same temperature range. β-$FeSi_2$, although possessing modest ZT values, is another useful material for power generation applications mostly because it is inexpensive.

At even higher temperatures, the most commonly used materials are Si-Ge alloys. The lattice thermal conductivity of the Si-Ge mixed crystals is significantly decreased by alloying compared to the pure Si and Ge. Si-Ge devices can operate with minimal performance degradation up to about 1300 K and have been used in power generators for various deep space missions.

In order to develop higher efficiency devices and systems, new thermoelectric materials with ZT > 1 must be identified. The limit for current materials over a wide range of temperature is ZT ~1 and the question is whether or not there is a limit on ZT. This question has been addressed theoretically and thermodynamic laws do not put any limits on ZT. For bulk materials, physical models have been developed to describe the transport coefficients included in the figure of merit in terms of valence and conduction band parameters. Using upper physical limits for some of these parameters, the ZT limit was estimated between 2 and 10.

3. New materials

Slack[3] has recently revisited the upper bound for ZT in bulk materials. A good thermoelectric material must combine a low lattice thermal conductivity with good electronic properties. It is therefore of interest to identify materials that possess lattice thermal conductivity comparable to amorphous materials. Slack suggested that the minimum thermal conductivity could be obtained when phonons have a mean free path equal to their wavelength. The minimum lattice thermal conductivity estimated based on this assumption is about 0.2 W/mK. Slack further suggested that crystals with complex structures containing loosely bonded atoms or molecules should possess low lattice thermal conductivity. Of course, the challenge is, once one has identified a crystalline material with a lattice thermal conductivity approaching the minimum theoretical value, to be able to optimize the electronic properties of this material in order to achieve large power factors. This is essentially linked to maximizing the parameter β introduced earlier. Slack called the ideal material combining a glass-like thermal conductivity and good electronic properties a phonon glass electron crystal (PGEC)[3]. While several materials are known to either have a glass-like thermal conductivity or excellent electronic properties such as Bi, the task is to identify material in which electronic and thermal properties can be decoupled and optimized separately. Slack listed several candidate materials that could potentially be PGEC materials. Considering an hypothetical material which would have the transport properties of Bi and a lattice thermal conductivity of 0.2 W/mK, Slack estimated a maximum dimensionless figure of merit of about 4 based on a band structure model. Although it might be quite difficult to develop such a material, the model shows that ZT values on the order to 2 and 3 may not be unrealistic.

Research efforts in the last 10 years have focused on two types of materials: bulk materials and low-dimensional structures. Many new bulk materials under investigation have complex crystal structures that often contain loosely bonded atoms that could be used as efficient phonon rattlers. Several new promising families of materials have been identified and encouraging results have been obtained. In low-dimensional materials, several approaches for increasing ZT have been proposed. Quantum size effects have been suggested to increase the power factor values in the in-plane direction of the films. In the cross-plane direction, one approach is to utilize the increased phonon scattering in superlattice interfaces to decrease the lattice thermal conductivity without degrading the electronic properties. Some of the recent developments for bulk materials are review in the following.

Among materials that present desirable attributes for the realization of a PGEC material is a class of materials called skutterudite, the prototype being $CoAs_3$. The interest in these materials for thermoelectric applications started in the 1950's and they have been revisited in the 1990's as potential high efficiency materials by researchers at the Jet Propulsion Laboratory and Dr. Slack at the Rensselaer Polytechnic Institute. For the last 10 years, intensive experimental and theoretical efforts worldwide have been started to further investigate the transport and other properties of numerous skutterudite materials including binary and ternary compounds, solid solutions, and filled compounds. Extensive reviews of these materials have been recently published in the literature[4,5]. Transport property studies for binary compounds showed that these materials possess attractive electronic properties but have a too high thermal conductivity to achieve large ZT values. Since then, efforts have mostly focused on "filled" skutterudites which is a version obtained by introducing additional ions inside the open structure. Filler ions have been successfully used to reduce the lattice thermal conductivity. The reduction was predominantly attributed to scattering of the phonons by the rattling of the loosely bound atoms in their "cages". The best ZT values to date for n-type materials was obtained for $CoSb_3$ (ZT ~ 0.85 at 1000K). For p-type materials, ZT ~1.4 was obtained at 1000K for $Ce(La)_yFe_{4-x}Co_xSb_{12}$ alloys[5]. ZT values for both n- and p-type materials are shown in Fig. 3 as a function of temperature.

Another material re-investigated recently for thermoelectric power generation is β-Zn_4Sb_3. Caillat et al.[6] have measured the thermoelectric properties of polycrystalline β-Zn_4Sb_3 samples. The electronic transport properties are typical of a semimetal with low electrical resistivity but with rather large Seebeck coefficient ~ 200 μV/K. The room temperature lattice thermal conductivity of 0.65 W/mK, nearly two times lower than that of Bi_2Te_3 alloys. The best ZT obtained to date on polycrystalline samples is about 1.4 at 675K[6] (see Fig. 3). Further optimization of the thermoelectric properties of this compound is however limited because of the difficulties to dope them and the restricted compositional variations possible.

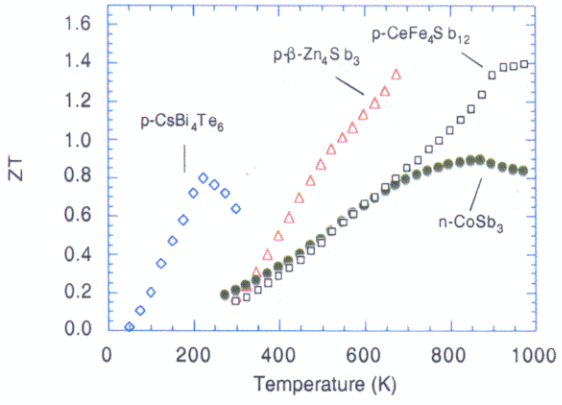

Fig. 3 ZT values for new thermoelectric materials.

An extensive effort at Michigan State University[7] has focused on a number of new chalcogenides composed mostly of heavy elements. They have identified a number of potential new materials for low temperature thermoelectric applications. A comprehensive review of these materials has recently appeared in the literature[7]. Perhaps the most promising compound identified to date is $CsBi_4Te_6$. This compound has a layered anisotropic structure with Cs ions between [Bi_4Te_6] layers. The α^2/ρ ratio can be maximized through doping and a maximum value of about 50 $\mu W/cmK^2$ was obtained at 185 K for the p-type material. The total thermal conductivity along the growth axis is about 1.5 W/mK at 300 K and is essentially constant down to 100 K. This atypical temperature dependence suggests that the "rattling" Cs ions significantly contribute to phonon scattering in this compound. The best ZT to date obtained along the needle direction is 0.82 for the p-type material (see Fig. 3), slightly better than p-type Bi_2Te_3 at this temperature. Whether or not this compound can be further optimized through doping and/or alloying will need to be investigated in the future as well as its mechanical stability to warrant its practical use in devices.

Other materials currently being investigated such as clathrates[8] and half-Heusler[9] alloys also possess attractive thermoelectric properties. ZT >1 may also be achieved for some of these materials with further optimization.

4. Segmented unicouples

Segmented thermoelectric unicouples incorporating advanced thermoelectric materials with superior thermoelectric figures of merit have been under development at the JPL since 1997[10-14]. These advanced segmented thermoelectric unicouples include a combination of state-of-the-art thermoelectric materials based on Bi_2Te_3 and novel materials developed at JPL. The optimal version of these segmented unicouples has a projected thermal to electrical efficiency of up to 15 % when operating at a cold-side temperature of 300K and a hot-side temperature 975K. The segmentation can be adjusted to accommodate various hot-side temperatures depending on the specific application envisioned. The segmented unicouple under development incorporates a combination of state-of-the-art thermoelectric materials and novel p-type Zn_4Sb_3, p-type $CeFe_4Sb_{12}$-based alloys and n-type $CoSb_3$-based alloys developed at JPL. The segmented unicouple is illustrated in Fig. 4. A semi-analytical approach based on the Swanson's model[15] has been used to optimize and calculate the expected properties and performance of the unicouple.

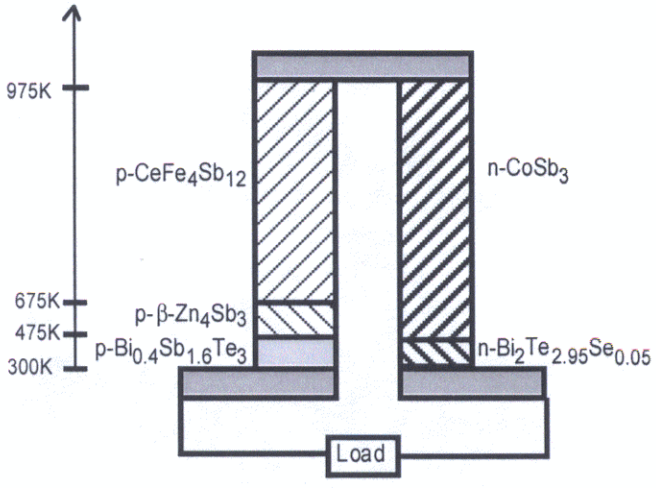

Fig. 4 Illustration of the advanced, segmented unicouple incorporating new high performance thermoelectric materials. The relative lengths of each segment and the cross-sectional areas for the p- and n-legs are drawn to scale.

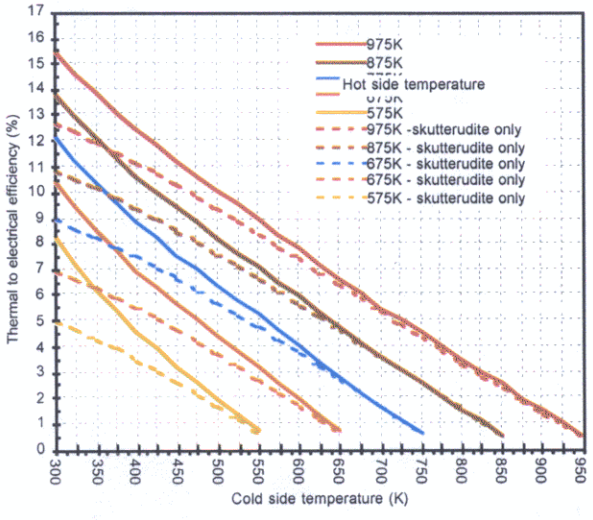

Fig. 5 Calculated thermal to electrical efficiency values for 2 different versions of the advanced unicouple: 1) fully segmented version as illustrated in Fig. 4 (solid lines) 2) skutterudite only legs as illustrated in Figure 3 (dashed lines). The maximum calculated thermoelectric efficiency is about 15%.

The maximum predicted thermal to electrical efficiency is about 15% for the fully segmented unicouple and for a cold and hot side temperatures of 300 and 975K,

respectively. Calculations have been performed for two different type of unicouples: 1) a fully segmented version as depicted in Fig. 4 2) a unicouple made of skutterudite-only legs (p-type $CeFe_4Sb_{12}$ and n-type $CoSb_3$). The major impact on the efficiency of the addition of Zn_4Sb_3 and Bi_2Te_3-based segments to the unicouple is clearly for lower cold-side temperatures. As the cold side temperature increases, the contribution of the lower segments to the overall thermal to electrical efficiency becomes smaller. Keeping the cold side temperature around room temperature may not be realistic in some actual systems and a skutterudite only unicouple may be of interest for some applications. The maximum thermal to electrical efficiency achievable for a skutterudite only unicouple operating at a hot-side temperature of 975K and a cold side temperature of 375K is about 11.5%.

Several versions of these unicouples are under development at JPL. Both skutterudite-only and segmented unicouples have been built. An experimental efficiency value on the order of 10% was demonstrated[16] on a skutterudite-only unicouple, in good agreement with theoretical predictions for the specific unicouple tested. While much development work remains to be performed before these unicouples can be used in actual thermoelectric generators, these initial results suggest that they might be useful high efficiency devices for a variety of applications.

Improved thermoelectric generators could be used in a variety of applications. Thermoelectric generators operating on natural gas, propane or diesel were built and used Bi_2Te_3 or PbTe alloys depending on the maximum hot side temperature (up to 873K)[17]. Despite their relatively low efficiency, these devices are used in various industrial applications because of their high reliability, low maintenance and long life, in particular when considering harsh environments. The most common applications are for cathodic protection, data acquisition and telecommunications. More recently, there has been a growing interest for waste heat recovery power generation, using various heat sources such as the combustion of solid waste, geothermal energy, power plants, and other industrial heat-generating processes. There is currently an important effort in Japan to develop large scale waste heat recovery thermoelectric generators using state-of-the-art materials[18]. But perhaps the automobile industry is the market with the most potential[19]. Because of the need for cleaner, more efficient cars, car manufacturers worldwide are interested in using the waste heat generated by the vehicle exhaust to replace or supplement the alternator. According to some car manufacturers, the available temperature range would be from 350 to 800K, which would be compatible with the new segmented unicouples. Advanced Radioisotope Power Systems (ARPSs) may be needed for several NASA missions planned over the next few years. These missions call for electrical power requirements ranging from 20 to 200 watts range and 6 to 15 years mission duration. The advanced segmented unicouples could be integrated into advanced RTGs, replacing the Si-Ge unicouples used until now. Preliminary estimates show that the resulting RTGs operating at a hot-side temperature of about 975K and rejection temperature of about 400K would have a high specific power (~8 We/kg) that is about twice that of the state-of-the-art RTGs and a high overall efficiency (> 12%), halving the $238PuO_2$ needed for a given electric power requirement. For example, only 4 GPHS bricks would be needed to provide 100We compared to 7 in a traditional RTG. With the exception of the radiator fins, minimal modifications of the Si-Ge RTGs design can be expected for integrating the advanced segmented unicouples into a more efficient system.

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